



NRL/MR/6170--96-7841

Experiences in Seeking Stabilizers for Zirconia Having Hot Corrosion-Resistance and High Temperature Tetragonal (t') Stability

ROBERT L. JONES

*Surface Chemistry Branch
Chemistry Division*

April 16, 1996

19960425 006

Approved for public release; distribution unlimited.

DTIC QUALITY INSPECTED 1

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE April 15, 1996	3. REPORT TYPE AND DATES COVERED Interim		
4. TITLE AND SUBTITLE Experiences in Seeking Stabilizers for Zirconia Having Hot Corrosion-Resistance and High Temperature Tetragonal (t') Stability		5. FUNDING NUMBERS PE - 61153 N PE - 62234 N		
6. AUTHOR(S) Robert L. Jones				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5320		8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6170-96-7841		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5660		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This report summarizes the results of a research effort aimed at identifying hot corrosion-resistant stabilizers for zirconia (ZrO ₂) which could be used in zirconia-based thermal barrier coatings (TBCs) for engines operating on marine fuel under seagoing conditions. Among the oxides investigated were TiO ₂ , CeO ₂ , Y ₂ O ₃ , MgO, Sc ₂ O ₃ , In ₂ O ₃ , and SnO ₂ . A brief overview of the hot corrosion of zirconia TBCs is given to illustrate the rationale used in evaluating the hot corrosion performance of the candidate oxides. The most promising stabilizer found for hot corrosion resistance was Sc ₂ O ₃ , or perhaps mixtures of Sc ₂ O ₃ and small amounts of Y ₂ O ₃ . It was also discovered that Sc ₂ O ₃ , Y ₂ O ₃ -stabilized ZrO ₂ (SYSZ), of ~ 7 mol% of total stabilizer of which 5-20% is Y ₂ O ₃ , shows improved 1400°C stability of the tetragonal (t') phase as compared to present-day Y ₂ O ₃ -stabilized ZrO ₂ TBC compositions. This new material may have potential for TBC use in future high temperature, high efficiency gas turbine engines.				
14. SUBJECT TERMS Thermal barrier coatings Zirconia Stabilization			15. NUMBER OF PAGES 23	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

CONTENTS

INTRODUCTION	1
RATIONALE OF SEARCH	3
INDIVIDUAL SYSTEMS	7
IMPROVED 1400°C TETRAGONAL (T') PHASE STABILITY WITH SCANDIA, YTTRIA-STABILIZED ZIRCONIA	12
POSSIBLE DEVELOPMENT OF SYSZ THERMAL BARRIER COATINGS ...	16
CONCLUSIONS	17
ACKNOWLEDGMENTS	17
REFERENCES	17

EXPERIENCES IN SEEKING STABILIZERS FOR ZIRCONIA HAVING HOT CORROSION-RESISTANCE AND HIGH TEMPERATURE TETRAGONAL (T') STABILITY

INTRODUCTION

Zirconia-based thermal barrier coatings (TBCs) are widely used in aviation gas turbines on such components as combustor cans, transition ducts, and 1st stage vane platforms and airfoils (1). By virtue of the thermal insulative properties of zirconia (ZrO_2), TBCs of only 125-250 μm zirconia thickness can reduce the temperature of the underlying metal by 100°C or more.

Thermal barrier coatings are produced by air plasma-spraying (APS) (1), or more recently, by electron beam-physical vapor deposition (EB-PVD) (2); they normally consist of a zirconia upper layer (125-250 μm) over an oxidation-resistant metallic bond coat (~125 μm), where the zirconia layer has either a porous "splatted-down semi-molten droplets" structure if prepared by APS, or a columnar grain structure if prepared by EB-PVD (Figs. 1 and 2). APS gives lower processing costs and somewhat better heat insulation, and is used mainly for combustors and large-area parts. EB-PVD gives superior spalling resistance, less air-cooling hole blockage, and a smoother, more aerodynamic upper surface, and therefore is preferred for blade and vane airfoils.

Another important distinction is in the mechanism of spalling failure. APS coatings appear to fail under oxidative thermal cycle conditions by the formation and linking-up of microcracks within the zirconia layer just above the bond coat interface (3). In contrast, EB-PVD coatings are thought to fail predominantly from cracks that develop, after some certain critical thickness/stress is reached, within the thermally grown oxide (TGO) that forms at temperature on the bond coat surface (4). Since, for given conditions, the rate of growth of the TGO film may be approximately predictable, it has been suggested that it may be possible to predict engineering lifetimes for EB-PVD thermal barrier coatings on critical components such as 1st stage blades where engine destruction might result in the event of massive TBC failure (4).

The prime thrust in gas turbine development over the years has been to

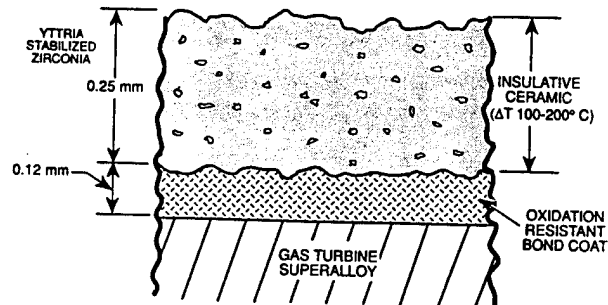


Figure 1 Cross-section of APS thermal barrier coating, indicating critical 5-15% porosity.

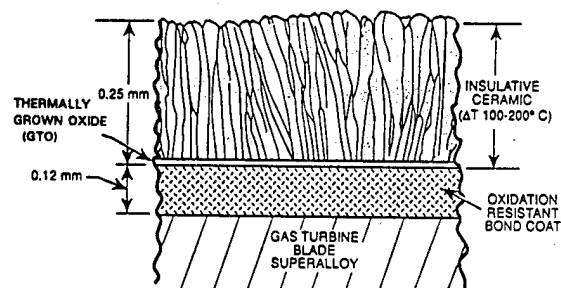


Figure 2 Cross-section of EB-PVD thermal barrier coating, indicating columnar grains and TGO layer.

continually increase the engine operating temperature, as usually characterized by the turbine inlet gas temperature. Numerous generations of superalloys have been produced at great expense, each with the objective of obtaining only another 25-30°C increase in engine temperature (Fig. 3). This process is becoming more and more difficult, however, because conventional cobalt- and nickel-based superalloys have been developed to very near their maximum temperature capability (which is ultimately limited by incipient melting).

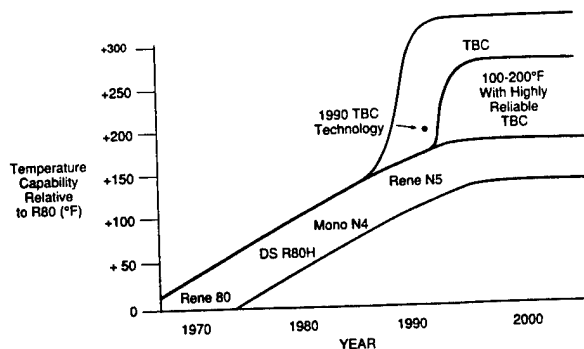


Figure 3 Superalloy temperature capability vs. highly reliable TBCs for GT blades. Used with permission of the General Electric Co., Ref. 5.

The appeal to engine manufacturers of the advanced use of TBCs in gas turbines is easy to understand since the 100°-150°C temperature advantage offered by TBCs is the equivalent of the expensive (and now even perhaps impossible) development of three new generations of airfoil superalloys (Fig. 3). A 100°C increase in gas temperature can significantly improve engine power and fuel economy. An increase of 200°F (110°C) in turbine inlet gas temperature, for example, allowed thrust to be increased from 40,000 lb to over 50,000 lb in jumbo-jet gas turbines (6). With regard to fuel economy, the use of TBCs on the blades of gas turbines is projected to save as much as 10 million gallons of fuel per year for a 250-aircraft fleet (7). In land-based gas turbines, a boost of 55°C (100°F) in turbine inlet temperature is expected to provide an 8 to 13 percent gain in power output, and a 1 to 4 percent increase in simple cycle efficiency (8). EB-PVD thermal barrier coatings are foreseen also, in certain aircraft operations, as giving an up to 3X improvement in 1st stage blade life (9).

Engine manufacturers are therefore seeking to perfect highly reliable TBCs for use at full thermal advantage on 1st stage blades, and in future ultra-high temperature, high efficiency engines. The first objective is aided by a NASA-sponsored project aimed at establishing a reliable model for predicting thermal barrier coating life on gas turbine blades (4). In the second goal, NASA research revealed some time ago that the current state-of-art yttria-stabilized TBCs do not have sufficient high-temperature phase stability (see below) for use at ultra-high (i.e., 1400°C) temperatures (10), which means that new TBC ceramics must be developed for ultra-high temperature TBCs to be viable.

The U.S. Navy has more than 140 ships, as listed in Table 1, which are powered by the General Electric LM2500 gas turbine, a derated and "marinized" version of the GE CF6 aviation gas turbine. These ships have vital missions, with those designated as AEGIS being the sophisticated, electronics-, detector-, and computer-laden ships responsible for the anti-missile defense of the carrier fleet. Increasing the speed, range, durability and economy of these ships by advanced use of TBCs in their gas turbine engines would be of great benefit to the Fleet; however, it is imperative that such TBCs operate reliably under battle conditions.

TABLE 1

U.S. Navy Ships Powered by
General Electric LM-2500 Gas Turbine Engines¹

<u>Class</u>	<u>Category</u>	<u>Number</u>	<u>Engines</u>	<u>Mission</u>
TICONDEROGA (AEGIS)	GM cruiser	27	4	hi-tech anti-missile/plane
BURKE (AEGIS)	GM destroyer	28	4	" " "
SPRUANCE	GM destroyer	31	4	anti-sub/plane/ship
KIDD	GM destroyer	4	4	anti-ship/plane
PERRY	GM frigate	50	2	anti-ship/plane/support
SUPPLY	fast support ship	4	4	modern fast supply/support
		144	476	

¹ from Jane's Fighting Ships, 1994-95; GM = Guided Missile

The critical problem in using TBCs in ship propulsion, as opposed to aviation, gas turbines is hot corrosion of the TBC by molten deposits formed in the engine from sea salt and marine fuel impurities (esp. sulfur and vanadium). The lower classes of marine fuel can contain up to 5 wgt% sulfur, and several hundred ppm of vanadium, whereas aviation fuel is limited to < 0.05 wgt% sulfur and no vanadium. Present Navy marine fuel specifications call for < 1.0 wgt% sulfur and no vanadium, but this level of purity can not necessarily be guaranteed in wartime emergency. There is the possibility also of heavy sea salt ingestion because of intake air filter damage during battle.

The current state-of-art TBC for aviation engines is comprised of Y_2O_3 (6-8wgt%)-stabilized ZrO_2 (YSZ), but, as shown initially by Kvernes *et al* (11), YSZ reacts strongly with vanadium impurities in marine fuel to form YVO_4 , with the TBC then failing because of Y_2O_3 depletion. Zirconia itself, on the other hand, exhibits good resistance to chemical reaction with vanadate-sulfate deposits (12,13). A search has therefore been made to find a reaction-resistant replacement stabilizer for Y_2O_3 that would yield a zirconia-based TBC for Navy ship propulsion engines as effective as YSZ thermal barrier coatings, but substantially more resistant to hot corrosion by marine fuel impurities, especially vanadium.

RATIONALE OF SEARCH

Critical TBC Phase Structure

Over the years it has been established that many factors are critical for a successful TBC including the macro-porosity of the APS zirconia layer (a certain minimum amount is required), the structure and composition of the bond coat, and the composition and "heat treatment" of the zirconia itself (1). In particular, the monoclinic-to-tetragonal phase transformation, which occurs at about 1180°C for pure ZrO_2 and involves a disruptive 4% volume change, must be avoided; this is accomplished by adding stabilizers such as MgO, CaO, or preferably, Y_2O_3 . Moreover, Stecura determined in NASA research that the best spalling performance (Fig. 4) occurred at 6-8 wgt% Y_2O_3 , i.e., at 3.4-4.5 mol% Y_2O_3 or 6.8-9.0 mol% $YO_{1.5}$ (14). This has been confirmed in service where YSZ coatings of Y_2O_3 (7-8wgt%)- ZrO_2 have been widely found to give the best thermal cycle life and engine performance.

Comparison with the ZrO_2 - Y_2O_3 phase diagram (Fig. 5) shows, however, that this composition does not lie in the fully stabilized cubic ZrO_2 region, but rather in the so-called partially stabilized zirconia (PSZ) region, where quenching from high temperature, as happens when thermal barrier

coatings are produced by APS or EB-PVD, yields the "nontransformable" tetragonal (t') zirconia phase. This phase is described as nontransformable since it does not undergo the catastrophic (in terms of TBC life) tetragonal (t) \rightleftharpoons monoclinic phase transformation that would otherwise occur with engine thermal cycling at this Y_2O_3 - ZrO_2 composition. It also, unlike the tetragonal (t) phase, is not transformed to monoclinic by physical stress. The t' phase has a complex microstructure containing many twins and antiphase-domain boundaries (15), and as discussed by Lelait and Alperine (16), it appears that this unique microstructure resists both grain growth, which inhibits phase transformation, and crack propagation, which confers thermomechanical toughness and spalling resistance to the TBC. All evidence to date indicates that, for optimal performance, a zirconia TBC must consist predominantly of the t' phase.

The critical zirconia t' phase necessary for good TBC performance can be destroyed, however, either by chemical attack or by high temperature aging. Removal of the Y_2O_3 stabilizer by YVO_4 formation during vanadium-induced hot corrosion, for instance, moves the YSZ composition into the low- Y_2O_3 region of the phase diagram (Fig. 5) where the t' phase is no longer possible. And as Miller *et al* (10) originally demonstrated, aging at 1200°C and above causes the metastable t' YSZ phase to revert to the equilibrium tetragonal (t) and cubic phases (Fig. 5), with the tetragonal (t) \rightleftharpoons monoclinic transformation then occurring upon subsequent thermal cycling.

Therefore, for Navy ship engine use, we must seek a new stabilizer which 1) yields the requisite zirconia t' phase, 2) has the chemical stability, when in solid solution in zirconia, to resist stabilizer depletion by corrosion reaction, and 3) provides a zirconia t' phase with good high temperature phase stability.

Modes of Attack on TBC

Molten salt deposits, especially those containing vanadium, can be quite wetting, and capable of penetrating through the zirconia TBC porosity down to the bond coat interface (Fig. 1). In such cases, even if the zirconia is totally "corrosion-proof," the TBC could still be degraded by bond coat corrosion, or by physical damage resulting from "freeze-thaw" of melt phases in the zirconia pores. Under what conditions zirconia penetration/bond coat corrosion may become troublesome has yet to

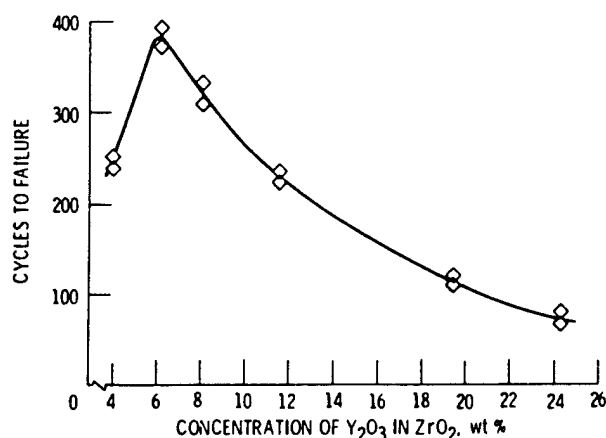


Figure 4 Effect of Y_2O_3 content on thermal cycle life of ZrO_2 - Y_2O_3 thermal barrier coating. Ref. 14.

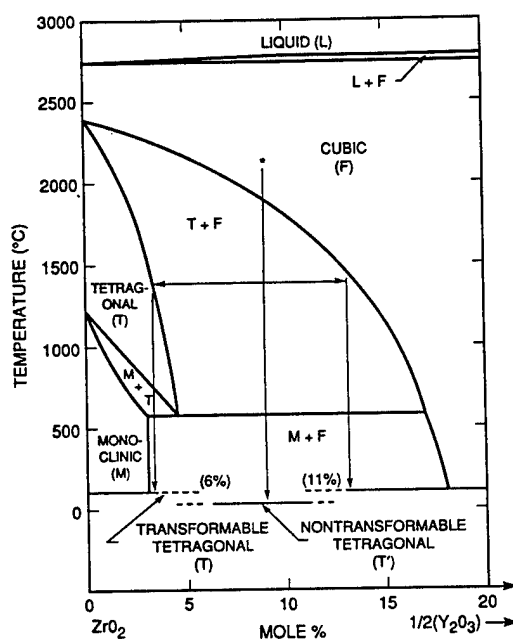
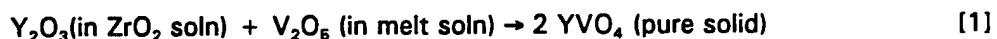


Figure 5 ZrO_2 - Y_2O_3 phase diagram, indicating t' formation, $t' \rightarrow t + c$ phase change at 1400°C, and $t \rightarrow m$ transformation on cooling, after Ref. 10.

be clearly determined. It was not seen, for example, in burner rig testing using high fuel contaminant levels of sulfur and sea salt (17), and of sulfur, vanadium and sea salt (18), where surface deposits were found, but there was no significant penetration of deposit into the zirconia, or bond coat corrosion.

Having a corrosion-resistant zirconia will therefore not guarantee a "corrosion-free" TBC; on the other hand, a corrosion-resistant TBC is not possible unless the ZrO_2 layer itself has strong resistance to vanadate-sulfate hot corrosion. In the present work, our efforts have been limited to seeking only a hot corrosion-resistant zirconia, and we have come to recognize in these efforts that there are at least three potential modes of degradation for stabilized zirconia, these being: chemical reaction, mineralization, and grain growth/phase transformation.

Chemical Reaction. In chemical attack, an identifiable product is formed, and usually a particular reaction can be postulated, e.g.,



The reaction of ceramic oxides with sodium vanadate compounds and V_2O_5 was shown to be largely driven by Lewis acid-base considerations (Fig. 6), with oxides that were neither too basic or too acidic being necessary to avoid reaction with melts of given Na_2O and V_2O_5 activities (13). This concept was the basis of our initial screening tests, wherein candidate oxides were mixed with $NaVO_3$ or $NaVO_3$ - V_2O_5 mixtures, heated at 700-900°C, and x-rayed to see if a vanadate product was formed. A number of oxides, including several rare earth oxides, were ruled out as potential stabilizers by this means.

Later we developed a thermogravimetric analysis/ SO_3 equilibrium technique (19,20) which allows the combined attack of the Na_2O - V_2O_5 - SO_3 melt components on ceramic oxides to be studied, and which provides a more quantitative "ranking" of the potential corrosion resistance of candidate oxides. An improved understanding of the thermochemistry of corrosive vanadate-sulfate melts was also obtained in these latter studies, including in some cases the determination of activity coefficients and standard Gibbs energies of formation (20). The oxides which performed well in these various chemical reaction tests were selected, more or less regardless of their perceived "stabilizing ability," for further study.

	— INCREASING ACIDITY —>		
	Na_3VO_4	$NaVO_3$	V_2O_5
Y_2O_3	NR	YVO_4	YVO_4
CeO_2	NR	NR	$CeVO_4$
ZrO_2	NR	NR	ZrV_2O_7 (BUT SLOWLY)
GeO_2	$Na_4Ge_9O_{20}$	$Na_4Ge_9O_{20}^{(*)}$	NR
Ta_2O_5	$NaTaO_3$	$Na_2Ta_4O_{11}$	α - $TaVO_5$
	NR = NO REACTION		
	(*) AS PPT FROM H_2O SOL'N		

Figure 6 Reaction of vanadium compounds with ceramic oxides, with no reaction (NR) occurring for compounds of similar Lewis basicities. Ref. 13.

Mineralization. In examining CeO_2 - ZrO_2 ceramics, we found that CeO_2 -stabilized ZrO_2 was readily destabilized by $NaVO_3$, even though neither CeO_2 or ZrO_2 reacts chemically with molten $NaVO_3$ (21). This was puzzling until it was recognized that the phases resulting from the destabilization, i.e., monoclinic ZrO_2 and cubic CeO_2 containing some ZrO_2 (21), were in fact the equilibrium phases in the CeO_2 - ZrO_2 system at 700-900°C (22). The molten $NaVO_3$ thus had acted as a "mineralizer." Mineralizers are substances which are not chemically reactive, but nonetheless facilitate the attainment of equilibrium in systems where phase transformation is sluggish (23); they are commonly used, e.g.,

in silica chemistry. Our experience with CeO_2 -stabilized ZrO_2 establishes that molten engine deposits may degrade TBCs not only by chemical reaction, but also by more subtle mineralization effects.

Grain Growth/Phase Transformation. Stabilized zirconias have been extensively researched, and the properties of the zirconia have been repeatedly found to depend critically upon the heat treatment and resultant grain size of the ceramic. Generally speaking, as temperature increases, so does grain growth, and therefore often the chance for undesirable phase transformation.

This is seen in the ZrO_2 - Y_2O_3 system. Yttria tetragonal (t) zirconia polycrystals (Y-TZP) is an important commercial ceramic used in extrusion dies, cutting instruments, machine tools, etc., because of its high strength and toughness. It is prepared by carefully heat-treating ZrO_2 containing 2-3 mol% Y_2O_3 in the range of 1400-1600°C and then cooling appropriately so as to retain the tetragonal (t) phase down to ambient temperature. However, if the grain size grows at temperature to exceed about 1 micron, the tetragonal (t) phase transforms spontaneously to the monoclinic phase upon cooling (15), resulting in a much weaker material. In contrast, the tetragonal (t') phase, perhaps because of its complex sub-grain microstructure, can withstand grain sizes of 100 microns or more without transformation.

Another aspect of the problem is the possibility of metastable zirconia phases at lower temperatures. Mixtures of ZrO_2 with various oxides will often exhibit a cubic or tetragonal structure after calcining at temperatures under 1000°C, and are therefore sometimes erroneously described as being "stabilized" by the given oxide. Sasaki *et al* (24) point out this difficulty by noting that, in their study of the ZrO_2 - $\text{InO}_{1.5}$ system, calcined powders of 20-50 mol% $\text{InO}_{1.5}$ consisted of only the tetragonal phase, whereas the true equilibrium phases below 1000°C were monoclinic ZrO_2 containing less than 1 mol% $\text{InO}_{1.5}$, and cubic $\text{InO}_{1.5}$ containing less than 1 mol% ZrO_2 . The equilibrium phases were achieved only upon the use of heat treatments of sufficient temperature and time to allow the excess $\text{InO}_{1.5}$ to segregate from the supersaturated ZrO_2 solution. Ceramicists therefore normally insist that a zirconia system must be fired at temperatures of 1500°C-1700°C and above to insure phase equilibrium, and to allow for possible grain growth and/or phase transformation, before it can be termed as stabilized or not.

On the other hand, zirconias are notoriously difficult to bring to phase equilibrium even at very high temperatures, and technically metastable zirconia phases, such as the metastable YSZ tetragonal (t') phase, could still prove useful in TBCs, perhaps especially in lower temperature engines. Discretion is obviously required in this area. Beyond this, and adding to the complexity of the problem, there is evidence that a significant difference may exist in the ultimate "stabilizing ability" of the various oxides (24,25).

Against this background, the various studies described below were undertaken. Most of the zirconias investigated were initially prepared as plasma spray powders of mean diameter of ~50 μm by a sol-gel procedure which gives excellent chemical homogeneity, and good uniformity of particle size without additional processing.

This investigation was preceded by a separate, NAVSEA-sponsored developmental research project, based primarily upon burner rig testing at the General Electric Aircraft Engine Co., which evaluated MgO -, Y_2O_3 -, and CeO_2 -stabilized ZrO_2 thermal barrier coatings for hot corrosion resistance to simulated vanadium, sulfur and sea salt contaminated marine fuel (26). While Y_2O_3 - and CeO_2 -stabilized ZrO_2 TBCs showed very good resistance (better than metallic coatings) to conventional molten sulfate hot corrosion, both suffered significant attack and degradation when from 5 up to 90 ppm of vanadium was added to the fuel. The essential findings from the GE-NAVSEA effort have been reported in the literature (18).

INDIVIDUAL SYSTEMS

Y₂O₃-ZrO₂

Although we are concerned over the potential hot corrosion of Y₂O₃-stabilized ZrO₂, YSZ in fact has tested, in both burner rig and engine experience, as superior to conventional metallic MCrAlY and aluminide blade coatings in resistance to molten sulfate-induced hot corrosion (11,27-29). The affinity of Y₂O₃ for reaction with V₂O₅ is the critical problem; this affinity is so strong that it precludes the use of Mg (which normally "ties up" the V₂O₅ as 3MgO.V₂O₅, or Mg₃V₂O₈, mp. 1100°C) for fuel vanadium treatment, since Y₂O₃ displaces MgO from Mg₃V₂O₈, as shown by Singhal and Bratton (30), by the reaction,



Since much experience, including our several laboratory studies (13,19,21,49,51) confirms the reaction of Y₂O₃ and YSZ with V₂O₅, it is not likely that YSZ will be useable with fuel containing significant vanadium.

MgO-ZrO₂

On the basis of reaction [2], MgO-stabilized ZrO₂ (MSZ) would be expected to be more resistant to vanadium fuel impurities than YSZ, and this appears indeed to have been found in marine engine service (11). However, MgO reacts readily with SO₃ to form melt-soluble MgSO₄, with the reaction of MgO in contact with molten NaVO₃ being demonstrable in the laboratory, for instance, even at very low partial pressures (10⁻⁷ bar) of SO₃ (19). Extensive formation of MgSO₄ leading to degradation of MgO-stabilized ZrO₂ TBCs in low-quality fuel burner rig tests has also been reported (12,18). Moreover, thermal cycling to only 1000°C/1050°C has been observed to cause progressive destabilization of MgO-stabilized ZrO₂, apparently as the result of rapid coarsening of the tetragonal MSZ grains followed by spontaneous tetragonal-to-monoclinic transformation (28). These shortcomings combine to make MgO-stabilized ZrO₂ an unpromising candidate for Navy ship engine applications.

CeO₂-ZrO₂

CeO₂-stabilized ZrO₂ (CSZ) has been patented as a hot corrosion resistant material (31). Laboratory tests also indicate CeO₂ to react less readily than Y₂O₃ with molten vanadate-sulfate systems (13,19,20). And there is evidence that plasma-sprayed CeO₂(25wgt%)-ZrO₂ yields a quenched-in, metastable tetragonal phase which is retained even after 100 hrs at 1600°C, and which does not undergo a tetragonal-monoclinic transformation under low temperature cycling (32). This latter material is proposed for ultra-high temperature TBCs, although the authors point out that it may be lacking in erosion resistance as compared to YSZ.

On the negative side, it appears, as noted above, that even in melts such as NaVO₃ where the V₂O₅ activity is too low for direct reaction, CSZ may nonetheless be destabilized by a mineralization effect. In burner rig tests with Na, S and V impurity additions, CSZ suffered chemical attack, forming both cerium sulfates (mostly in the lower temperature tests at 700°C) and CeVO₄; it was difficult to be certain, perhaps because of the high V and S levels used, that CSZ was significantly more resistant than YSZ to hot corrosion in these particular tests (18). For these reasons, and because CSZ is being actively researched by several groups around the world, we have not pursued CeO₂-stabilized ZrO₂ further in this Navy effort.

TiO₂-ZrO₂

Titania is a moderately acidic oxide and, at the lower TiO₂ compositions, the available ZrO₂-TiO₂ phase diagrams are similar to the ZrO₂-Y₂O₃ system, which raised the possibility of TiO₂-stabilized ZrO₂ (if it exists) as a corrosion-resistant TBC. In chemical tests, TiO₂ did not react chemically with either NaVO₃ or V₂O₅, but its crystal structure was converted from anatase to rutile (the equilibrium structure for TiO₂), indicating a mineralization effect. Moreover, when vanadate-corrosion tests of TiO₂-ZrO₂ ceramics rapidly cooled from the melt by a proprietary method were conducted, the ceramics were transformed from their original tetragonal or cubic structure to a predominantly monoclinic structure, but with no apparent reaction product. This indicated that TiO₂-ZrO₂ is probably subject to destabilization by "mineralization" in the same way as CeO₂-ZrO₂. Also, TiO₂ was found to react directly with Na₂SO₄ to give Na₂TiO₃ and SO₃, with TiO₂-stabilized ZrO₂ therefore being possibly susceptible to molten sulfate hot corrosion. Accordingly, research on TiO₂-ZrO₂ was halted.

It is interesting, and perhaps relevant, that Pandolfelli *et al* (33) have since attempted unsuccessfully to produce TiO₂-ZrO₂ tetragonal zirconia polycrystals (TZP). Although powders of 17.9 and 21.5 mol-% TiO₂ were 100% tetragonal after calcining at 950°C, these powders invariably, when densified at temperatures above 1200°C, underwent the tetragonal-monoclinic transformation on cooling, making it impossible to retain TZP at room temperature. Pandolfelli *et al* concluded that TiO₂ additions to ZrO₂ suppressed densification, and accelerated grain growth so that the critical grain size for spontaneous tetragonal-monoclinic transformation was exceeded before satisfactory densification could be achieved.

SnO₂-ZrO₂

Vanadium in crude oil causes vanadate-type corrosion of the rare earth-exchanged Y zeolite (REY) catalysts used in high temperature (500°C-800°C) fluid-cracking petrochemical refining. Tin oxide (SnO₂) suppresses the vanadium attack possibly because, as we have shown, SnO₂ is inert at these temperatures to chemical reaction with all sodium vanadates and even V₂O₅ itself, and so may be retained in the Y zeolite structure to support the zeolite crystallinity and catalytic activity (31). Later work confirmed that SnO₂ was inert also to combined Na₂O-V₂O₅-SO₃ attack (32).

This suggested SnO₂ as a possible corrosion-resistant stabilizer for ZrO₂. No accepted phase diagram for SnO₂-ZrO₂ is available, and SnO₂ was not known to stabilize ZrO₂. On the other hand, it was reported that 10 mol-% SnO₂ was soluble in ZrO₂, and reduced the tetragonal-to-monoclinic phase transformation temperature from 1200°C to 1050°C (36). Another paper indicated that SnO₂(3mol%), Y₂O₃(1.5mol%)-ZrO₂ could be successfully sintered at 1400°C to give a tetragonal phase of 0.25 microns grain size, although their goal of adding SnO₂ to obtain a tetragonal phase of high Y₂O₃ content (e.g., 6 mol-% Y₂O₃) was not achieved (37).

In our research, sol-gel prepared powders of 5-20 mol-% SnO₂ in ZrO₂ were all found to decompose into separate monoclinic ZrO₂ and crystalline SnO₂ phases upon calcining at 900°C. However, Qadri *et al* (38) obtained stabilization of the cubic ZrO₂ phase over the composition range of 3-20 wgt-% (2.5-17 mol-%) SnO₂ in ZrO₂ for thin films deposited by electron beam-physical vapor deposition on substrates heated at 300°C. A limited sulfate hot corrosion burner rig test at 900°C was made using specimens having thin films of SnO₂-ZrO₂ "top-coated" as additional protection onto a conventional MCrAlY protective metallic coating. One specimen pin survived 1000 hrs with little attack, but two others were severely corroded, indicating a certain "touchiness" of the system. It is thus doubtful, especially considering the high (for a ceramic) volatility and ease of reduction of SnO₂, that a SnO₂-ZrO₂ ceramic of sufficient robustness to survive as a high-temperature gas turbine TBC can be developed, although use for corrosion protection at lower temperatures may be possible.

In₂O₃-ZrO₂

Next to SnO₂, In₂O₃ shows the greatest resistance to V₂O₅ and SO₃-Na₂SO₄ reaction of all the oxides tested (19,39). Although the In₂O₃-ZrO₂ system has been little studied, In₂O₃ appears to stabilize ZrO₂ (24), and to yield the tetragonal (t') phase when quenched from the cubic phase region for compositions in the range of 5-12 mol-% In₂O₃ (40). However, In₂O₃ has a significant vapor pressure (for a ceramic), and has been found to volatilize from sintered (ZrO₂)_{0.8}(In₂O₃)_{0.4} and (ZrO₂)_{0.6}(In₂O₃)_{0.6} specimens at temperatures above 1400°C (41). On the other hand, In₂O₃-ZrO₂ ceramics have been successfully fired at up to 1700°C (24,40), and one might expect less volatilization of In₂O₃ at lower In₂O₃ compositions, perhaps especially from the quenched tetragonal (t') phase.

Our investigation of In₂O₃-stabilized ZrO₂ (ISZ) was conducted before the references above (24,40) were available, and centered on a study of the vanadate corrosion resistance of a sol-gel prepared In₂O₃(3.9mol%)-ZrO₂ powder which was calcined at 900°C (39). This ISZ powder was destabilized by even pure NaVO₃, despite the fact that In₂O₃ itself is chemically inert to NaVO₃ with up to 20 mol-% of V₂O₅ added. However, the rate of destabilization was less than for yttria-stabilized zirconia, and in that sense, ISZ was an improvement over YSZ. Only free In₂O₃ was detected during ISZ destabilization in melts of up to V₂O₅(20mol%)-NaVO₃, whereas only InVO₄ was found for melts of V₂O₅(35mol%)-NaVO₃ and higher. Destabilization thus apparently occurred by mineralization in the low-V₂O₅ melts, but by chemical reaction (or mineralization followed by chemical reaction) in the high-V₂O₅ melts.

When air plasma-spraying (APS) of ISZ thermal barrier coatings was attempted, the In₂O₃ vaporized out, leaving a coating of only monoclinic ZrO₂. It was subsequently demonstrated, however, that ISZ coatings could be prepared by e-beam deposition, with 3.5-11 mol-% In₂O₃ stabilizing the cubic ZrO₂ structure (42). A study was also made of a series of "dual" In₂O₃,Y₂O₃-stabilized ZrO₂ powders in hope of combining the phase stabilizing strength of Y₂O₃ with the corrosion resistance of In₂O₃ but, although better than YSZ, these powders too were readily destabilized by NaVO₃ melts, especially at 900°C (43).

In retrospect, it appears that the 900 °C firing temperature and 3.9 mol-% In₂O₃ composition (chosen by "analogy" with the Y₂O₃-ZrO₂ system) used in our original study of ISZ were not optimum. ZrO₂ containing 8-10 mol-% In₂O₃, and heat treated and quenched from 1500-1700°C to obtain the tetragonal (t') phase, would most likely be the best candidate for a vanadate-resistant ISZ ceramic. We are undertaking a final, short study of ISZ to explore this possibility.

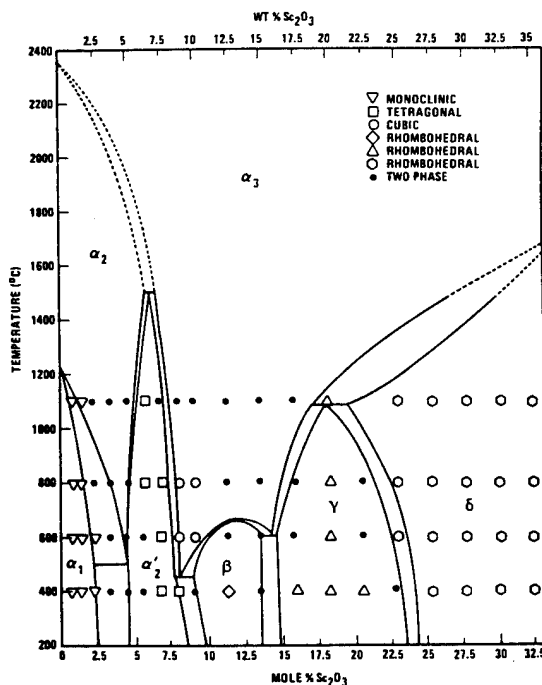


Figure 7 ZrO₂-Sc₂O₃ phase diagram, after Ruh et al. Ref. 45.

Sc₂O₃-ZrO₂

The high temperature properties of scandia (Sc₂O₃) are sufficiently good (e.g., its vapor pressure is lower than Al₂O₃ or CeO₂) that Sc₂O₃ is one of the few oxides recommended for consideration for engine use above 1650°C (44). The phase diagram by Ruh *et al* (45) for ZrO₂-Sc₂O₃ (Fig. 7) indicates that, in the region of about 4 to 8 mol% Sc₂O₃, a tetragonal α_2' zirconia phase is stable down to 200°C. This phase has since been identified by Sheu *et al* (40) as being the metastable tetragonal (t') phase. The desired tetragonal (t') phase thus appears readily obtainable in the ZrO₂-Sc₂O₃ system.

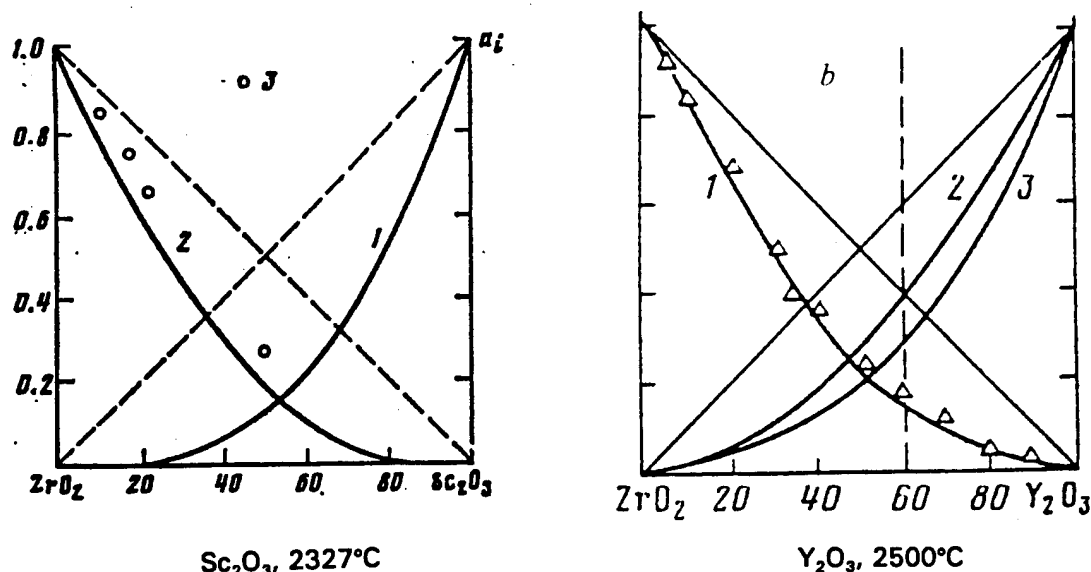


Figure 8 Comparison of the activity of Y₂O₃ and Sc₂O₃ in solid solution in high temperature ZrO₂, as compiled in a review by Jacobson (46) of high temperature oxide properties, after Refs. 47,48.

The Russian literature, as compiled by Jacobson (46), suggests also (Fig. 8) that Sc₂O₃ exhibits a strong negative deviation from ideal solid solution behavior in ZrO₂ at 2327°C in the region of 0 to 20 mol% Sc₂O₃ (47). This indicates attractive forces between ZrO₂ and Sc₂O₃ (i.e., tending toward a stable phase). Since negative deviations from ideal solution behavior normally become stronger as the temperature is lowered, this predicts the possibility of a chemically highly-stable (i.e., low Sc₂O₃ activity) ZrO₂-Sc₂O₃ phase at lower temperatures. The high temperature negative deviation from ideal solid solution behavior in ZrO₂ appears to be somewhat greater for Sc₂O₃ than Y₂O₃ (48).

As an opposing consideration, Belov *et al* observed that all of the Sc₂O₃ was volatilized from a 50 mol% Sc₂O₃-ZrO₂ specimen after only 100 minutes at 2327°C (47). Both Sc₂O₃ and Y₂O₃ volatilize incongruently, with data gathered by Jacobson (46) indicating a temperature of 1440°C for a vapor pressure of 10⁻¹² atm for the major fragment ScO over pure Sc₂O₃, as opposed to 1470°C for 10⁻¹² atm of the major fragment YO over pure Y₂O₃. The vapor pressures would be reduced for solid solutions of 4 to 7 mol% of Y₂O₃ or Sc₂O₃ in ZrO₂, with the Sc₂O₃ vapor pressure then being possibly the lower because of the stronger deviation from ideal solid solution behavior shown in Fig. 8.

Our experiments showed Sc₂O₃ to be more resistant than Y₂O₃ to reaction with an SO₃/Na₂SO₄ environment (49), and also to reaction with molten NaVO₃. This last point was somewhat difficult to

establish because a weak $3\text{NaVO}_3 \cdot \text{Sc}_2\text{O}_3$ compound forms below 880°C (50) whose x-ray diffraction pattern is very similar to, and thus difficult to distinguish from, unreacted Sc_2O_3 . However at 900°C , Sc_2O_3 can be readily determined to be chemically inert to NaVO_3 , whereas Y_2O_3 reacts strongly, with YVO_4 formed. Subsequently Sc_2O_3 -stabilized ZrO_2 (SSZ) was prepared, and confirmed to be superior to Y_2O_3 -stabilized ZrO_2 in vanadate-corrosion resistance, both as sintered pellets (49), and as an air plasma-sprayed coating on test coupons, where the SSZ coating withstood heavy deposits of highly V_2O_5 -rich (up to 70 mol% V_2O_5) NaVO_3 melts at 900°C (Fig. 9) without destabilization (51).

In follow-up developmental research, SSZ thermal barrier coatings were successfully prepared by APS at several different plasma-spraying facilities, and by electron beam-physical vapor deposition in the General Electric EB-PVD production coater. The coatings were laid down using essentially the same parameters as developed for YSZ, and showed equivalent coating efficiencies and similar granular structures to YSZ in each case. The problem of spalling (actually a "lifting off" of the entire SSZ layer) that was encountered in vanadate-corrosion testing of our first SSZ coated coupons (ref. 51, and as noted in Fig. 9) was not seen in any of the subsequent coating procedures, and thus was presumably an artifact just of that one test set. It should not be necessary to develop radically new coating procedures or equipment in order to replace YSZ coatings with scandia-stabilized zirconia TBCs.

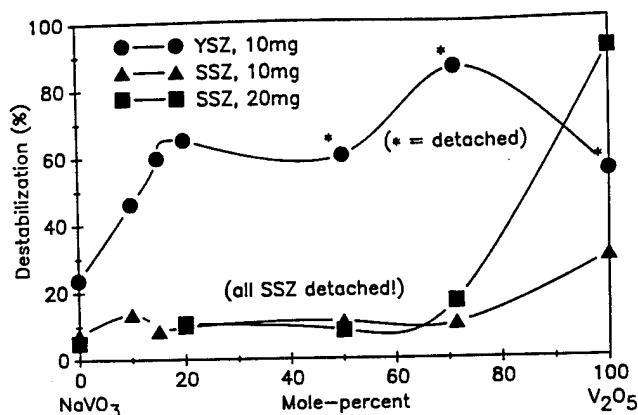


Figure 9 Destabilization of SSZ vs. YSZ coated coupons by V_2O_5 - NaVO_3 at 900°C , as a function of V_2O_5 mol% of the deposit. Ref. 51.

Two performance tests have been thus far completed. One test, conducted in cooperation with the Naval Engine Airfoil Center (NEAC), Cherry Point, NC, was of low pressure plasma-sprayed (LPPS) SSZ vs. YSZ thermal barrier coatings on the HP 2nd stage vanes of a Harrier gas turbine engine in accelerated test-cell trials (i.e., only oxidation, no hot corrosion). The SSZ and YSZ coatings both spalled in this test (possibly because of lack of optimization of the exploratory LPPS coating process), but with the SSZ coating being perhaps somewhat less, or at least no worse, spalled than the YSZ coating. The second test was of SSZ thermal barrier coated pins in a long-term 1700°F , high-sulfur (up to 4% sulfur, but no vanadium) burner rig evaluation of TBCs at the General Electric Aircraft Engine Co, Cincinnati, OH. In this test, the SSZ coating withstood 1750 hrs without spalling or monoclinic formation, although trace amounts of $\text{Zr}_3\text{Sc}_4\text{O}_{12}$ were detected by x-ray (52). However, YSZ coatings withstood the Na_2SO_4 -high SO_3 burner rig environment equally well, with no spalling or destabilization, and there was thus no evidence that SSZ was more corrosion-resistant than YSZ.

In general, the consensus has been that "SSZ tests about as good, but not discernibly better than YSZ." This judgment is somewhat mitigated by noting 1) that prototype SSZ coatings were being compared with highly optimized YSZ coatings developed over many years, and 2) that no good tests involving vanadium, where SSZ might show its worth, have yet been obtained.

Moreover, a new factor has quite recently come into the scandia-stabilized zirconia question; this being that we have found that scandia, yttria-stabilized zirconia (SYSZ) may retain its tetragonal (t') phase stability up to 1400°C (53,54). This is a 200°C higher temperature capability than current YSZ coatings provide and, if proven, could make SYSZ coatings of potential importance to the entire gas turbine industry.

IMPROVED 1400°C TETRAGONAL (t') PHASE STABILITY WITH SCANDIA, YTTRIA-STABILIZED ZIRCONIA

Current superalloys have a temperature capability of 1100°C and, if we presume a ΔT of up to 300°C across the TBC may be possible, then there may be applications even in the near future where the outer surface of the TBC will be at 1400°C (55). This is well beyond the tetragonal (t') stability range of present-day Y_2O_3 -stabilized ZrO_2 TBCs (10,55), and accordingly, there is currently a vigorous search for ultra-high temperature TBC zirconias.

An accepted procedure in this search is to heat the candidate TBC coating or material isothermally for 100 hrs at high temperature, and then to analyze by x-ray for the phase transformations, especially monoclinic formation, that occur on slow cooling, or in subsequent thermal-cycle thermal expansion measurements. By this test, Brandon *et al* proved that CeO_2 (25 wgt%)- ZrO_2 could survive 100 hrs at 1600°C without detectible monoclinic formation, and was thus a candidate ultra-high temperature TBC material, although it may have less erosion resistance than YSZ coatings (32,56).

Besides ceria, hafnia (HfO_2) is being considered as a means of improving ultra-high temperature TBC capability. Miller and Leissler have examined HfO_2 - Y_2O_3 TBCs and found that they give equivalent performance to ZrO_2 - Y_2O_3 TBCs, but at high Y_2O_3 compositions of up to 27 wgt% where the crystal structure is fully cubic. There is thus no need for tetragonal (t') stability, and Miller suggests that HfO_2 - Y_2O_3 may therefore be useful as an ultra-high temperature TBC (57).

Ibegazene *et al* (58) have investigated HfO_2 from another aspect, working on the hypothesis that substitution of HfO_2 into the ZrO_2 matrix might move the phase transformations to higher temperatures (in accord with the HfO_2 - Y_2O_3 phase diagram), and so improve ultra-high temperature TBC performance. Using 8 wgt% Y_2O_3 stabilizer, they obtained the tetragonal (t') phase for all ZrO_2 - HfO_2 mixtures ranging from 0 to 100% HfO_2 . However, 100-hr isothermal aging tests at 1200°C revealed that HfO_2 in fact accelerated the rate of tetragonal (t') reversion, with substantial amounts of the monoclinic phase being found with the 50 and 100 percent HfO_2 coatings. Ibegazene *et al* propose that HfO_2 indeed moves the $c \rightleftharpoons t'$ transformation, which they believe normally occurs at 1400-1500°C with Y_2O_3 (8wgt%)- ZrO_2 (although this lies well within the mixed tetragonal (t)-cubic phase region), to higher temperatures; they conclude, however, that, since the t' phase is now presumably more unstable at 1200°C by virtue of being further from its new, higher $c \rightarrow t'$ transformation temperature, the ultimate effect may be to actually increase the driving force for, and therefore the rate of, the tetragonal (t') phase reversion.

Evidence for High-temperature t' Stability with Sc_2O_3 , Y_2O_3 -stabilized ZrO_2

Experimental Series 1. In experiments intended to examine the vanadate hot corrosion resistance of Sc_2O_3 , Y_2O_3 -stabilized ZrO_2 (SYSZ), a series of sol-gel prepared zirconia plasma spray powders having nominally 7 wgt% of total stabilizer, and in which the stabilizer was varied from 0 to 100% Sc_2O_3 , were fired for 140 hrs at 1400°C, and then cooled in-furnace (maximum rate of cooling 10°C/minute) overnight (53). The compositions of the powders, as determined by ECP emission spectroscopy, are listed in Table 2.

The behavior of these powders in terms of the percent of monoclinic formation (i.e., destabilization of the tetragonal phase) is compared in Fig. 10 as a function of the percent of the stabilizer that is Sc_2O_3 . For this comparison, it was deemed sufficient to estimate the percent of monoclinic formation simply by the ratio of the relative peak heights, i.e.,

$$\% \text{ monoclinic} = \frac{\text{Mono. } (\bar{1}11) \text{ Peak Hgt}}{(\text{Mono. } (\bar{1}11) \text{ PH} + \text{Tetr. } (111) \text{ PH})} \quad [3]$$

TABLE 2

Composition of Series 1 SYSZ Powders as Determined by Inductively Coupled Plasma Emission Spectroscopy

Powder number	Composition (mol%)				Stabilizer percent*	Total percent**
	ZrO ₂	HfO ₂	Y ₂ O ₃	Sc ₂ O ₃	Sc ₂ O ₃	Y ₂ O ₃ + Sc ₂ O ₃
1	94.9	1.20	3.90	0.0	0.0	3.90
2	94.7	1.33	3.37	0.63	15.8	4.00
3	94.3	1.35	2.80	1.55	35.6	4.35
4	93.8	1.33	1.88	2.94	61.0	4.82
5	93.0	1.31	0.93	4.78	83.7	5.71
6	92.7	1.33	0.37	5.63	93.8	6.00
7	92.8	1.29	0.0	5.90	100.0	5.90

*Mole percent of Sc₂O₃ in stabilizing oxide.

**Total mole percent of stabilizing oxide.

The powder behaviors shown in Fig. 10 are for the powders simply as calcined at 900°C (●); for the powders after being aged for 140 hrs at 1400°C (○); for the powders after being aged and then exposed for 100 hrs at 900°C in a 50 wgt% mix with NaVO₃ (▽); and for the powders after being aged for 140 hrs at 1400°C, heavily ground in a mortar and pestle, and then exposed for 100 hrs at 900°C in a 50 wgt% mix with NaVO₃ (□).

Fig. 10 reveals several important points. First, Powder 1 (only Y₂O₃ stabilizer), and Powders 5-7 (high Sc₂O₃- to 100%-Sc₂O₃ stabilizer) are 100% tetragonal (or cubic) and show no monoclinic peaks after being calcined at 900°C; however, after 140 hrs at 1400°C, the monoclinic phase is formed, and ranges, as calculated by Eqn. 3, from about 32% for Powder 1 down to 13% for Powder 6. Examples of the different x-ray spectra over the range of 27-36° 2-theta are shown in Fig. 11. If the monoclinic content is calculated more quantitatively, following the method of Toraya *et al* (59), then Powder 1 is indicated to have a monoclinic volume content of about 53%, and Powder 6 about 17%.

Since the composition of Powder 1 at 3.90 mol% Y₂O₃ (or 7.80 mol% YO_{1.6}) lies near the center of the mixed tetragonal (t)-cubic phase region at 1400°C in the ZrO₂-Y₂O₃ phase diagram (Fig. 5), the equilibrium phase composition at 1400°C would be approximately 50% each of the tetragonal (t) and cubic phases. Our finding of ~50 vol% monoclinic for Powder 1 at 25°C is therefore consistent with the t' → t + c phase reaction having gone to completion at 1400°C, and the tetragonal (t) → monoclinic transformation having gone to completion upon cooling to 25°C.

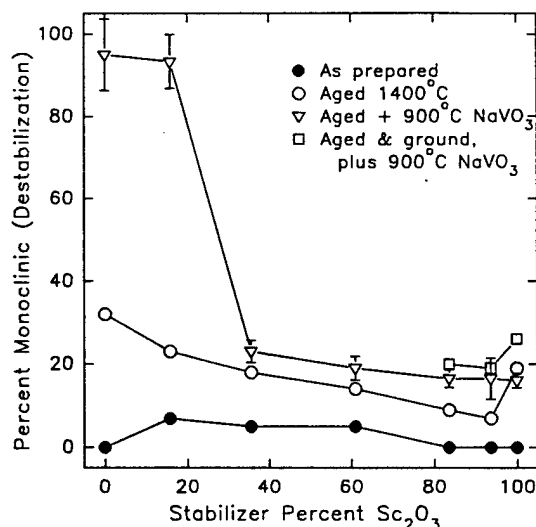


Figure 10 Percent monoclinic formation of SYSZ powders as function of stabilizer Sc₂O₃ percent (cf. Table 2), and the various treatments indicated.

Most importantly, it can be clearly seen in Fig. 10 that the amount of monoclinic formed upon 1400°C aging decreases in going from Powder 1, Y_2O_3 (3.9mol%)- ZrO_2 , to Powder 6, Sc_2O_3 (5.63mol%), Y_2O_3 (0.37mol%)- ZrO_2 , but then increases slightly for Powder 7, Sc_2O_3 (5.90mol%)- ZrO_2 . This is strong evidence, on the basis of the reasoning above, that the tetragonal (t') reversion at 1400°C, $t' \rightarrow t + c$, is substantially slower for Sc_2O_3 -stabilized ZrO_2 containing small additions of Y_2O_3 than for either purely Y_2O_3 - or purely Sc_2O_3 -stabilized ZrO_2 .

The second point to be noticed in Fig. 10 is that, when the 1400°C-aged powders were corrosion-tested with 900°C NaVO_3 , the Y_2O_3 -rich Powders 1 and 2 were converted essentially to 100% monoclinic (because the Y_2O_3 was removed by YVO_4 formation), whereas the remainder of powders, which contained ~40 relative % and upwards of Sc_2O_3 in the stabilizer, showed virtually no additional development of monoclinic in the presence of molten NaVO_3 . This suggests that SYSZ ceramics may have, in the same material, the potential for giving both improved vanadate hot corrosion resistance, and superior 1400°C tetragonal (t') phase stability, as compared to YSZ thermal barrier coatings. This hypothesis must be conditioned, however, by noting that it has not been verified, as with, e.g., Powder 3 (2.8 mol% Y_2O_3 , 1.55 mol% Sc_2O_3), that the Y_2O_3 and Sc_2O_3 are truly acting in synergy to provide hot corrosion resistance, and that it is not just the Sc_2O_3 alone giving corrosion-resistant stabilization, while the Y_2O_3 behaves only as a reactable impurity.

The final point of importance in Fig. 10 is that the 1400°C-aged Powders 5-7 show little, if any, gain in monoclinic content either upon being heavily ground in a mortar and pestle, or when the ground Powders are subsequently subjected to molten NaVO_3 corrosion-testing. This indicates 1) that the tetragonal phase is not transformed by physical stress and therefore is most likely the tetragonal (t') phase, and 2) that grinding, or physical abrasion, does not cause an increase in susceptibility to vanadate corrosion.

Experimental Series 2. To confirm these findings, a second series of SYSZ powders was prepared by the same sol-gel processing, but this time aiming at 7 mol% total stabilizer content, and

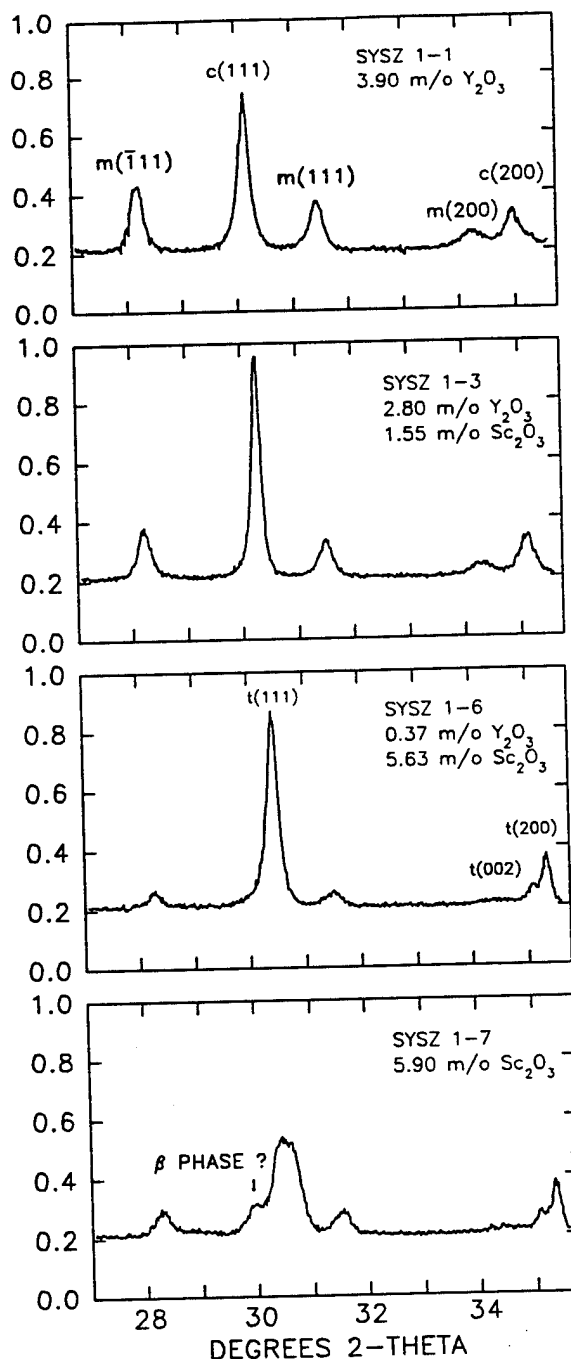


Figure 11 X-ray diffraction spectra of Series 1 SYSZ powders after aging at 1400°C for 140 hrs.

examining only the range of 100 to 80 relative percent of Sc_2O_3 to better pinpoint the optimum stabilizer composition (cf. Table 3, p. 16). The powders were aged for 140 hrs at 1400°C in just the same way as the Series 1 SYSZ powders.

Fig. 12 shows the x-ray diffraction spectra in the $27\text{--}36^\circ$ 2-theta region for the different Series 2 SYSZ powders after the 1400°C aging.

The 1400°C stability of the SYSZ tetragonal (t') phase is reconfirmed by the x-ray spectra of the Series 2 powders. Very minimal monoclinic formation is indicated for Powders 3-5, where the stabilizer is 95%, 90%, and 80% Sc_2O_3 , respectively. The total stabilizer content is ~ 6.75 mol% for the Series 2 powders, as opposed to ~ 6.0 mol% for the equivalent Series 1 powders; it appears, from a comparison of the two sets of spectra, that the higher stabilizer content is probably better.

Potential SYSZ Thermal Barrier Coatings

In considering Sc_2O_3 , Y_2O_3 -stabilized ZrO_2 for possible development as a thermal barrier coating system, it is useful to briefly review some of the factors involved.

Scandium lies just above yttrium in Group IIIB of the periodic table, and Sc_2O_3 is very similar to Y_2O_3 in having high resistance to reduction under low O_2 partial pressures, and low vapor pressure at very high temperatures. In these properties, Sc_2O_3 is substantially superior to CeO_2 . Sc_2O_3 also exhibits a strong negative deviation from ideal solid solution behavior in ZrO_2 at high temperature (47), and thus should tend to form strong chemical bonding in the ZrO_2 matrix. The ability of Sc_2O_3 to stabilize the tetragonal (t') phase has been established (40,45). Finally, Sc_2O_3 (sp. dens. 3.86) has the advantage of being lighter than Y_2O_3 (sp. dens. 5.01), ZrO_2 (sp. dens. 5.6) or HfO_2 (sp. dens. 9.68).

With regard to processing, it has been shown that Sc_2O_3 -stabilized ZrO_2 TBCs can be successfully prepared by APS or EB-PVD using

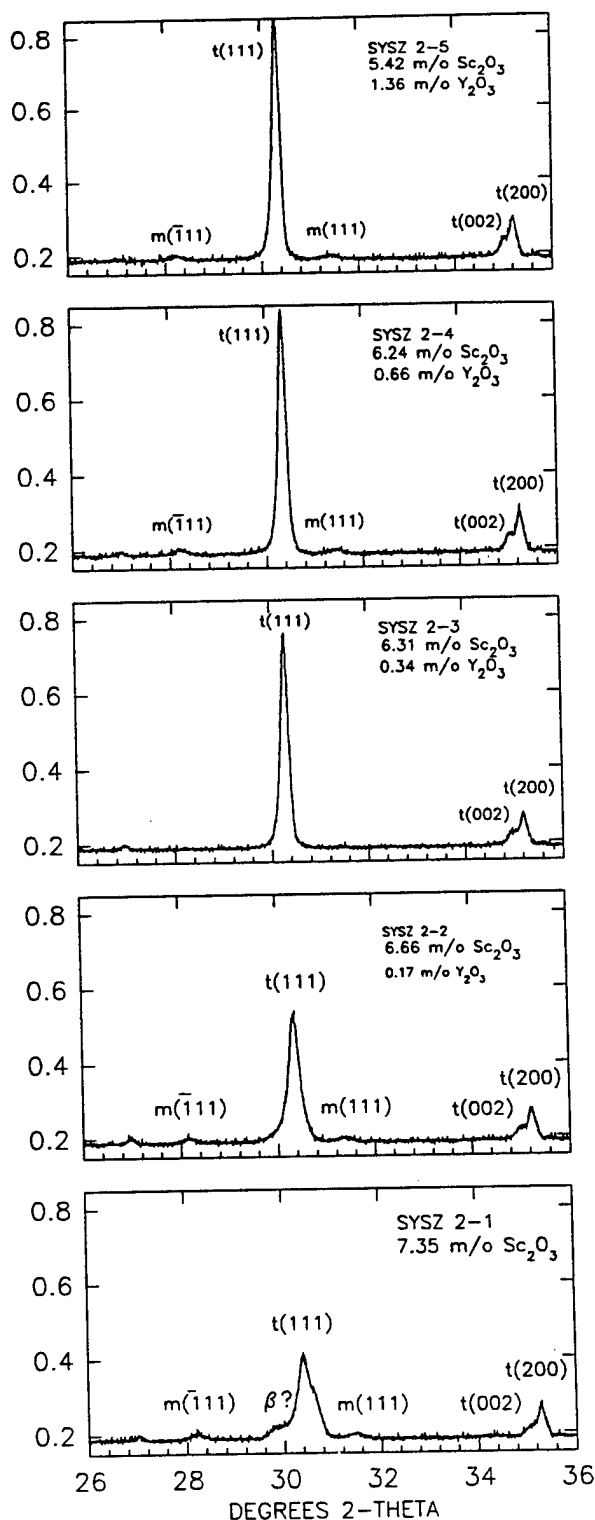


Figure 12 X-ray diffraction spectra of Series 2 SYSZ powders after aging at 1400°C for 140 hrs.

TABLE 3

Composition of Series 2 SYSZ Powders as Determined by
Inductively Coupled Plasma Emission Spectroscopy

Powder number	Composition (mol%)				Stabilizer percent*	Total percent**
	ZrO ₂	HfO ₂	Y ₂ O ₃	Sc ₂ O ₃	Sc ₂ O ₃	Y ₂ O ₃ + Sc ₂ O ₃
1	91.75	0.90	0.0	7.35	100.0	7.35
2	92.22	0.95	0.17	6.66	97.5	6.83
3	92.38	0.97	0.34	6.31	94.9	6.65
4	92.14	0.95	0.66	6.24	90.4	6.90
5	92.26	0.96	1.36	5.42	79.9	6.78

*Mole percent of Sc₂O₃ in stabilizing oxide.

**Total mole percent of stabilizing oxide.

essentially the same parameters as for Y₂O₃-stabilized ZrO₂. There is no a priori reason to expect difficulty in producing SYSZ thermal barrier coatings, especially since Sc₂O₃ and Y₂O₃ have similar vapor pressures. The erosion resistance of TBCs depends critically upon the processing parameters, especially for APS, but again because of the similarity of Sc₂O₃ and Y₂O₃, there is no reason to believe that the erosion resistance of SYSZ coatings should be significantly poorer than YSZ coatings.

Cost of Sc₂O₃ A principal objection raised against Sc₂O₃-stabilized ZrO₂ TBCs is the cost of Sc₂O₃, which is presently of the order of \$5/gm for bulk purchases. Prices for Sc₂O₃ are dropping, however, with Sc₂O₃ of 99% purity from China recently being offered for \$0.80/gm. To coat an area of 60 cm² (the approximate area, front and back, of a 1st stage vane or blade airfoil in an engine of the size of the LM2500) with a Sc₂O₃(7mol%)-ZrO₂ layer of 250 mμ thickness requires ~0.58 gms of Sc₂O₃. Depending on price, the additional cost for Sc₂O₃ would thus be from about \$0.46 to \$3.00 per blade. Since modern air-cooled gas turbine blades cost of the range of \$1000-\$3000 each, and the TBC coating itself perhaps \$100-\$200, the small extra cost for Sc₂O₃ would be easily recovered by improvements of well less than 1% in TBC performance or component lifetime. The cost effectiveness of Sc₂O₃ would be especially great in those cases where SYSZ might allow TBCs to be used in corrosive environments, such as ship propulsion engines, or ultra-high temperature applications, which YSZ coatings are not capable of withstanding.

The analysis above neglects the loss of material during the coating process. As little as 20% of the zirconia may be deposited on the work piece as a TBC coating in APS, and perhaps as little as 5% in EB-PVD. However, the zirconia overspray must be ultimately recovered even if for, as at present, only the cleaning of the APS spray booth or EB-PVD evaporator. If expensive Sc₂O₃-containing zirconias come into use, it should be relatively easy to arrange for salvage of the valuable overspray material.

POSSIBLE DEVELOPMENT OF SYSZ THERMAL BARRIER COATINGS

The development of a new thermal barrier coating system is an expensive and complex matter that must be approached with caution, especially for TBCs that may be used on critical engine components such as 1st stage blades. It is not even certain, for example, that the improved high-temperature tetragonal (t') phase stability found here for SYSZ plasma spray powders will be retained in TBCs prepared by APS from these materials, although experience with Y₂O₃-stabilized ZrO₂ indicates that the crystal structure of the TBC is usually in fact benefited by the APS process (60).

As an initial step toward development of SYSZ thermal barrier coatings, we plan to work with industry to prepare SYSZ thermal barrier coated test coupons. The coupons will then be examined in a specialized test system capable of heating the SYSZ outer surface to 1400°C while keeping the coupon metal substrate at 1100°C or lower. These tests will provide critical data on the overall performance of SYSZ at high temperature, including spalling, tetragonal (t') phase stability, sintering (sintering of the zirconia is a looming problem in high temperature TBCs), and bond coat oxidation. From these data, it should be possible to assess the ultimate potential of Sc_2O_3 , Y_2O_3 -stabilized ZrO_2 as a high temperature TBC.

CONCLUSIONS

Of the oxides (Y_2O_3 , MgO , CeO_2 , TiO_2 , SnO_2 , In_2O_3 and Sc_2O_3) evaluated, Sc_2O_3 is the most corrosion-resistant effective stabilizer for ZrO_2 , and Sc_2O_3 -stabilized ZrO_2 (SSZ) the most promising candidate for thermal barrier coating (TBC) use in Navy ship propulsion gas turbines burning marine-quality fuel.

Sc_2O_3 , Y_2O_3 -stabilized ZrO_2 (SYSZ), of ~7 mol% total stabilizer content of which 5-20% is Y_2O_3 , shows both superior hot corrosion resistance (especially against vanadate hot corrosion), and improved 1400°C tetragonal (t') phase stability, as compared to present-day Y_2O_3 -stabilized ZrO_2 thermal barrier coatings.

SYSZ may be an important new candidate for ultra-high temperature TBC use in future high temperature, high efficiency gas turbines.

ACKNOWLEDGMENTS

This research was sponsored partly by the Office of Naval Research, with Dr. A. J. Sedriks as Scientific Officer, and partly under the ONR-NRL Advanced Materials Transition Project directed by Dr. D. U. Gubser. The support is gratefully acknowledged.

I wish also to thank P. Knapp and G. Simpson, of the Naval Engine Airfoil Center, and B. Nagaraj and D. Wortman, of the General Electric Aircraft Engine Co., for their help and encouragement in this effort.

REFERENCES

1. R. A. Miller, "Current Status of Thermal Barrier Coatings -- An Overview," Surface and Coatings Technol., **30** 1-11 (1987).
2. T. E. Strangman, "Thermal Barrier Coatings for Turbine Airfoils," Thin Solid Films, **127** 93-105 (1985).
3. R. A. Miller and C. E. Lowell, "Failure Mechanisms of Thermal Barrier Coatings Exposed to Elevated Temperatures," Thin Solid Films, **95** 265-273 (1982).
4. S. M. Meier, D. M. Nissley and K. D. Sheffler, "Thermal Barrier Coating Life Prediction Model Development," NASA Contractor Report 189111, NASA Lewis Research Center, Cleveland, OH, (July, 1991).
5. B. A. Nagaraj, D. V. Wortman and N. Lindblad, General Electric Aircraft Engine Co., Private Communication, (Nov., 1992). Used with permission of the General Electric Aircraft Engine Co., Cincinnati, OH.

6. W. P. Danesi and M. Semchyshen, "The Future in Superalloys," in The Superalloys, ed. C. T. Sims and W. C. Hagel, pgs. 565-574, J. Wiley & Sons, New York (1972).
7. S. M. Meier, D. K. Gupta and K. D. Sheffler, "Ceramic Thermal Barrier Coatings for Commercial Gas Turbine Engines," J. of Minerals (JOM), **43(3)** 50-53 (1991).
8. W. P. Parks, E. E. Hoffman, W. Y. Lee and I. G. Wright, "Thermal Barrier Coatings Issues in Advanced Land-Based Gas Turbines," in Proc. of Thermal Barrier Coating Workshop, pgs. 35-47, NASA Conf. Publ. 3312, NASA Lewis Research Center, Cleveland, OH (1995).
9. S. Bose and J. DeMasi-Marcin, "Thermal Barrier Coating Experience in Gas Turbine Engine at Pratt & Whitney," in Proc. of Thermal Barrier Coating Workshop, pgs. 63-77, NASA Conf. Publ. 3312, NASA Lewis Research Center, Cleveland, OH (1995).
10. R. A. Miller, J. L. Smialek and R. G. Garlick, "Phase Stability in Plasma-Sprayed, Partially Stabilized Zirconia-Yttria," in Science and Technology of Zirconia, Advances in Ceramics, Vol. 3, ed. A. H. Heuer, pgs 241-253, The American Ceramic Society, Westerville, OH (1981).
11. I. Kvernes, J. K. Solberg and K. P. Lillerud, "Ceramic Coatings on Diesel Engine Components," in Proc. of 1st Conf. on Advanced Materials for Alternative Fuel Capable Directly Fired Heat Engines, ed. J. W. Fairbanks and J. Stringer, pgs. 233-257, CONF-790749, DOE, Washington, DC (1979).
12. R. J. Bratton, S. K. Lau, C. A. Andersson and S. Y. Lee, "Studies of Thermal Barrier Coatings for Heat Engines," in Proc. of 2nd Conf. on Advanced Materials for Alternative-Fuel-Capable Heat Engines, ed. J. W. Fairbanks and J. Stringer, pgs. 6-82 - 6-117, RD-2369-SR, EPRI, Palo Alto, CA (1982).
13. R. L. Jones, C. E. Williams and S. R. Jones, "Reaction of Vanadium Compounds with Ceramic Oxides," J. Electrochem. Soc., **133** 227-230 (1986).
14. S. Stecura, "Optimization of the NiCrAl-Y/ZrO₂-Y₂O₃ Thermal Barrier System," NASA Tech. Memo. 86905, NASA Lewis Research Center, Cleveland, OH (1985).
15. A. H. Heuer, R. Chaim and V. Lanteri, "Review: Phase Transformations and Microstructural Characterization of Alloys in the System ZrO₂-Y₂O₃," Science and Technology of Zirconia III, Advances in Ceramics, **24A** 3-20 (1988).
16. L. Lelait and S. Alperine, "T.E.M. Investigations of High Toughness Non-Equilibrium Phases in the ZrO₂-Y₂O₃ System," Scripta Metallurgica et Materialia, **25** 1815-1820 (1991).
17. B. A. Nagaraj, A. F. Maricocchi, D. J. Wortman, J. S. Patton and R. L. Clarke, "Hot Corrosion Resistance of Thermal Barrier Coatings," Tech. Paper 92-GT-44, ASME, New York, NY (1992).
18. B. A. Nagaraj and D. J. Wortman, "Burner Rig Evaluation of Ceramic Coatings with Vanadium-Contaminated Fuels," Trans. of the ASME, **112** 536-542 (1990).
19. R. L. Jones, "Thermogravimetric Study of the 800°C Reaction of Stabilizing Oxides with SO₃-NaVO₃," J. Electrochem. Soc., **139** 2794-2799 (1992).
20. R. F. Reidy and R. L. Jones, "Thermogravimetric Analysis of the Reaction of CeO₂ with the NaVO₃-SO₃ System," J. Electrochem. Soc., **142** 1353-1357 (1995).

21. R. L. Jones and C. E. Williams, "Hot Corrosion Studies of Zirconia Ceramics," Surface and Coatings Technol., **32** 349-358 (1987).
22. E. Tani, M. Yoshimura and S. Somiya, "Revised Phase Diagram of the System $\text{ZrO}_2\text{-CeO}_2$ Below 1400°C ," J. Am. Ceram. Soc., **66** 506-510 (1983).
23. M. Yoshimura, "Phase Stability of Zirconia," Ceramic Bull., **67** 1950-1955 (1988).
24. K. Sasaki, P. Bohac and L. J. Gauckler, "Phase Equilibria in the System $\text{ZrO}_2\text{-InO}_{1.5}$," J. Am. Ceram. Soc., **76** 689-698 (1993).
25. T.-S. Sheu, T.-Y. Tien and I.-W. Chen, "Cubic-to-Tetragonal (t') Transformation in Zirconia-Containing Systems," J. Am. Ceram. Soc., **75** 1108-1116 (1992).
26. "Ceramic Coating Development for Marine Gas Turbine Components," conducted by General Electric Aircraft Engine Co. under NAVSEA Contract N00167-86-C-0135, 1986-1990.
27. W. D. Grossklaus, G. B. Katz and D. J. Wortman, "Performance Comparison of Advanced Airfoil Coatings in Marine Service," in Proc. of Symp. on High Temperature Coatings, ed. M. Khobaib and R. C. Krutenat, pgs. 67-83, The Metallurgical Society, Warrendale, PA (1986).
28. I. Kvernes, "Ceramic Coatings as Thermal Barriers in Diesel and Gas Turbine Engine Components," in High Tech Ceramics, Part C, Materials Science Monographs, **38C**, ed. P. Vincenzini, pgs. 2519-2536, Elsevier, Amsterdam (1987).
29. D. J. Wortman, B. A. Nagaraj and E. C. Duderstadt, "Thermal Barrier Coatings for Gas Turbine Use," Mats. Sci. and Engr., **A121** 433-440 (1989).
30. S. C. Singhal and R. J. Bratton, "Stability of a $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ Thermal Barrier Coating in Turbine Fuel with Contaminants," Trans. of the ASME, **102** 770-775 (1980).
31. P. A. Siemers and D. W. McKee, U.S. Patent 4,328,285 (1982).
32. J. B. Brandon, R. Taylor and P. Morrell, "Microstructure, Composition and Property Relationships of Plasma-Sprayed Thermal Barrier Coatings," Surface and Coatings Technol., **50** 141-149 (1991).
33. V. C. Pandolfelli, J. A. Rodrigues and R. Stevens, "Effects of TiO_2 Addition on the Sintering of $\text{ZrO}_2\text{-TiO}_2$ Compositions and on the Retention of the Tetragonal Phase of Zirconia at Room Temperatures," J. of Materials Sci., **26** 5327-5334 (1991).
34. R. L. Jones, "Oxide Acid-Base Reactions Relating to the Inhibition of Vanadium Attack on REY Zeolite Catalysts," J. of Catalysis, **129** 269-274 (1991).
35. R. L. Jones, "Resistance of Tin Dioxide to Chemical Reaction with Vanadate-Sulfate Melts," J. Am. Ceram. Soc., **76** 1635-1637 (1993).
36. G. Wilson and F. P. Glasser, "Solid Solution in the $\text{ZrO}_2\text{-SnO}_2\text{-TiO}_2$ System," Trans. of British Ceramic Soc., **88(3)** 69-74 (1989).
37. D. Bingham, C. A. Leach and B. C. H. Steele, "Effect of Additions of TiO_2 , SnO_2 , and Al_2O_3 on Electrical Properties of Tetragonal Zirconia," Materials Sci. and Technol., **3(6)** 401-403 (1987).

38. S. B. Qadri, E. F. Skelton, M. Z. Harford, C. Kim and P. Lubitz, "Electron-Beam Deposition of $\text{ZrO}_2\text{-SnO}_2$ Films," Surface and Coatings Technol., **63** 155-157 (1994).
39. R. L. Jones and D. Mess, "India as a Hot Corrosion-Resistant Stabilizer for Zirconia," J. Am. Ceram. Soc., **75** 1818-1821 (1992).
40. T.-S. Sheu, J. Xu and T.-Y. Tien, "Phase Relationships in the $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{-In}_2\text{O}_3$ Systems," J. Am. Ceram. Soc., **76** (1993) 2027-2032.
41. L. V. Morozova, P. A. Tikhonov, O. V. Egorova and V. B. Glushkova, "Evaporation Processes of Indium Oxide from $\text{ZrO}_2\text{-In}_2\text{O}_3$ System Ceramic Composites," J. of Applied Chemistry, USSR, **62** 884-886 (1989).
42. S. B. Qadri, E. F. Skelton, M. Z. Harford, R. Jones and P. Lubitz, "e-Beam Deposition of In_2O_3 Stabilized ZrO_2 Films," J. Vac. Sci. Technol., **A9** 510-511 (1991).
43. R. L. Jones, R. F. Reidy and D. Mess, "Vanadate Hot Corrosion Behavior of India, Yttria-Stabilized Zirconia," J. Am. Ceram. Soc., **76** 2660-62 (1993).
44. N. J. Shaw, J. A. DiCarlo, N. S. Jacobson, S. R. Levine, J. A. Nesbitt, H. B. Probst, W. A. Sanders and C. A. Stearns, "Materials for Engine Applications Above 3000°F -- An Overview," Tech. Memo. 100169, NASA-Lewis Research Center, Cleveland, OH (1987).
45. R. Ruh, H. J. Garrett, R. F. Domagala and V. A. Patel, "The System Zirconia-Scandia," J. Am. Ceram. Soc., **60(9-10)** 399-403 (1977).
46. N. S. Jacobson, "Thermodynamic Properties of Some Metal Oxide-Zirconia Systems," NASA Tech. Memo. 102351, NASA Lewis Research Center, Cleveland, OH (Dec., 1989).
47. A. N. Belov, G. A. Semenov, G. A. Teterin and T. M. Shkol'nikova, "Evaporation and Thermodynamic Properties of Sc_2O_3 and of $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ Binary Solid Solutions According to High-Temperature Mass Spectrometry Data. II. Calculations," Russ. J. Physical Chemistry, **61(4)** 468-470 (1987).
48. A. N. Belov and G. A. Semenov, "Thermodynamics of Binary Solid Solutions of Zirconium, Hafnium and Yttrium Oxides from High-Temperature Mass Spectrometry Data," Russ. J. Physical Chemistry, **59(3)** 342-344 (1985).
49. R. L. Jones, "Scandia-Stabilized Zirconia for Resistance to Molten Vanadate-Sulfate Corrosion," Surface and Coatings Technol., **39/40** 89-96 (1989).
50. V. H. Schwarz and L. Schmidt, "New Compounds with Garnet Structure. VI. Vanadates," Z. anorg. allg. Chem., **413** 150-164 (1975).
51. R. L. Jones, "Hot Corrosion Resistance of Scandia Stabilized Zirconia Coatings," in Corrosion and Corrosive Degradation of Ceramics, Ceramics Trans. Vol. 10., ed. R. E. Tressler and M. McNallan, pgs. 291-308, The American Ceramic Society, Westerville, OH (1990).
52. B. A. Nagaraj, R. L. Jones and D. Mess, "Evaluation of Ceramic Thermal Barrier Coatings in Burner Rigs with Contaminated Fuels", Paper A3.06. Presented at the Intl. Conf. on Metallurgical Coatings and Thin Films, San Diego, CA, (26 April, 1994).

53. R. L. Jones and D. Mess, "Scandia,Yttria-Stabilized Zirconia for Thermal Barrier Coatings," Surface Science and Technol., accepted for publication.
54. R. L. Jones and D. Mess, "Improved Tetragonal Stability at 1400°C with Scandia,Yttria-Stabilized Zirconia," to be presented at the 1996 Intl. Conf. on Metallurgical Coatings and Thin Films, San Diego, CA, April 22-26, 1996.
55. J. R. Brandon and R. Taylor, "Phase Stability of Zirconia-Based Thermal Barrier Coatings. Part I. Zirconia-Yttria Alloys," Surface and Coatings Technol., **46** 75-90 (1991).
56. J. R. Brandon and R. Taylor, "Phase Stability of Zirconia-Based Thermal Barrier Coatings. Part II. Zirconia-Ceria Alloys," Surface and Coatings Technol., **46** 91-101 (1991).
57. R. A. Miller, "Thermal Barrier Coatings for Aircraft Engines -- History and Directions," pgs. 17-34, NASA Conf. Publ. 3312, NASA Lewis Research Center, Cleveland, OH (1995).
58. H. Ibegazene, S. Alperine and C. Diot, "Yttria Stabilized Hafnia-Zirconia Thermal Barrier Coatings (Influence of Hafnia Addition on TBC Structure and High Temperature Behavior), presented at the 1993 ASME Winter Annual Meeting, New Orleans, LA (Nov. 28 - Dec. 3, 1993).
59. H. Toraya, M. Yoshimura and S. Somiya, "Quantitative Analysis of Monoclinic-Stabilized Cubic ZrO₂ Systems by X-Ray Diffraction," J. Am. Ceram. Soc., **67** C183-C184 (1984).
60. T. A. Taylor and R. E. Taylor, "Testing of Stability and Thermal Properties of Thermal Barrier Coatings," in ASM Handbook Vol 5. Surface Engineering, eds. C. A. Cotell et al, pgs. 654-659, ASM International, Materials Park, OH (1994).